ELECTRON SPIN–LATTICE RELAXATION OF Cu(II) IN Zn(II)-BIS(DIETHYL-DISELENOCARBAMATE) SINGLE CRYSTALS

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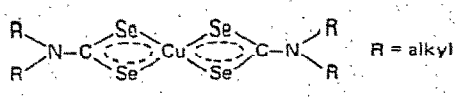
Using the pulse saturation method the spin–lattice relaxation rate T_1^{-1} for Cu(II) in Zn(II)-bis(diethyl-diselenocarbamate) was measured in the temperature range $1.5 < T < 33$ K. From the T-dependence of T_1^{-1} the Debye temperature of the host crystal was obtained. The angular dependence of T_1^{-1} as well as the influence of the hyperfine interaction on T_1^{-1} are discussed.

1. Introduction

EPR investigations on single crystals and powders of Cu(II)–bis(dialkyl-diselenocarbamates) $Cu(desc)_2$(I) diamagnetically diluted in various host lattices [1–5] showed some interesting features: (a) very small line widths of the Cu hfs lines, (b) non-coinciding principal axes of the g- and the ^{63,65}Cu-hfs tensors and (c) a very high degree of covalency in the Cu–Se bonds.



(I)

In this paper we report detailed investigations of the electron spin–lattice relaxation in single crystals of $Cu(desc)_2$, diamagnetically diluted by the corresponding Zn(II) complex, in order to explain the line width behaviour. Possible influences of the covalency on the spin–lattice relaxation will also be discussed qualitatively. Until now there has been no information on the spin–lattice relaxation of ions of the iron group in crystals with very covalent metal–ligand bonds except for an investigation of the phonon bottleneck effect in Cu(II)–maleonitril-dithiolate single crystals [6].

2. Experimental

$Cu(desc)_2$ and $Zn(desc)_2$ were obtained as described earlier [7,8]. Single crystals containing about 1.5% of the copper complex were grown by slow evaporation of a chloroformic solution of both complexes. Both $Zn(desc)_2$ and $Cu(desc)_2$ form monoclinic crystals, space group $P\,2_1/c$, with four molecules in the unit cell [9]. In each case two of these are centro-symmetrically related, forming dimeric units. The local symmetry on the Zn atom can be considered as a distorted tetrahedron, that of the Cu atom is pyramidal. As suggested by Keijzers [5], in the diluted state the copper complex does not accept the structure of the pure Zn-complex, but has a structure which resembles strongly that of the pure $Cu(desc)_2$.

Single crystal EPR spectra were recorded on an X-band spectrometer THN-251 (Thomson, France) and on a superheterodyne spectrometer at $\nu = 28.9$ GHz in the temperature range 4.2–295 K. The magnetic field was controlled by an NMR-marker; polycrystalline DPPH was used as the g-marker.